

Determination of Heat Capacity from DSC or Calorimetry measurements

INTRODUCTION

The heat capacity C_p of a sample is defined as : $C_p = \left(\frac{\partial H}{\partial T} \right)_p$.

- If the heat capacity is calculated per mole of sample, it will be named “molar heat capacity” and its value will be expressed in $\text{J.mol}^{-1}.\text{K}^{-1}$.
- If the heat capacity is calculated per mass unit of sample (e.g. per gram), it will be named “specific heat capacity” or eventually “massic heat capacity” and its value will be expressed in $\text{J.g}^{-1}.\text{K}^{-1}$.
- If the heat capacity is calculated per volume unit of sample (e.g. per mL), it will be named “volumic heat capacity” and its value will be expressed in $\text{J.mL}^{-1}.\text{K}^{-1}$.

Three different methods can be used for the determination of heat capacity : the continuous (§1), the stepwise (§2) and the drop (§4) methods.

The first two methods can be used for C_p determination of solids and liquids materials.

The drop method can be only used for solids materials.

For C_p determination of liquids please refer to §3.

1. Continuous method

Instruments calibrated by Joule effect (3D CALVET type sensor) :

This method can only be applied to instruments calibrated by Joule effect such as CALVET, CALVET PRO, CALVET CRYO, MICROCALVET, MICROCALVET ULTRA ...

The method consists in performing two runs with two vessels : the measuring vessel and the reference vessel. The first run is performed with the two empty vessels (blank test), the second run with a mass m_s of sample in the measuring vessel. Each run consists in a isotherm at a temperature T_i , a heating between the initial temperature T_i and a final temperature T_f at constant heating rate β and a isotherm at the final temperature T_f (Figure 1).

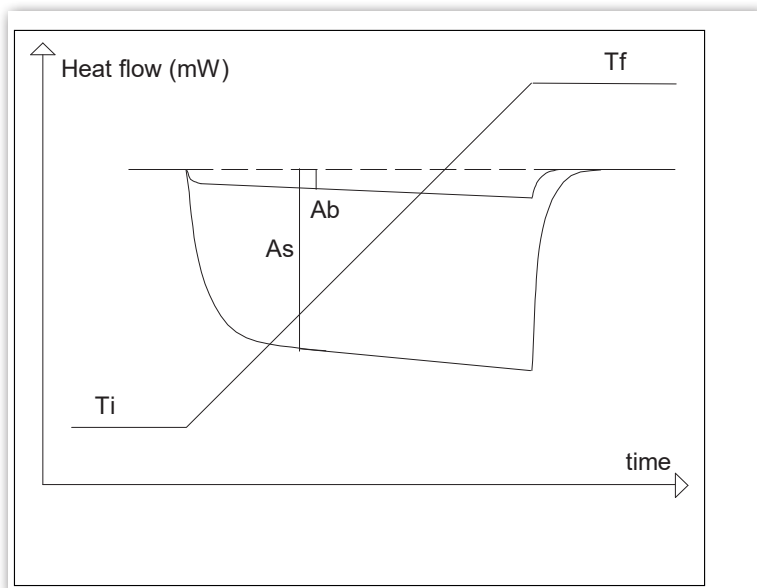


Fig. 1 : continuous method

If A_b and A_s are the amplitudes of the Heatflow signals measured with the blank and with the sample respectively, the value of specific heat capacity C_p is :

$$C_p = \frac{A_s - A_b}{m_s \times \beta} \quad (1)$$

with C_p in $\text{J.g}^{-1}.\text{K}^{-1}$ A_s and A_b in W m_s in g β in K.s^{-1}

Note :

- The isothermal sections of the curves must be long enough in order to obtain a stable signal before and after each heating.

Instruments calibrated by a standard material :

Other types of instruments such as SETLINE DSC, THEMYS ONE, THEMYS and other analyzers based on plate DSC are usually calibrated by the melting of standards. This calibration method is suitable for thermal events such as melting or phase transition, but is generally not accurate enough for C_p measurement. In the case of C_p determination, the calibration must be done by using a standard material with a known heat capacity.

The method consists in performing three runs with two crucibles : the measuring and the reference crucibles.

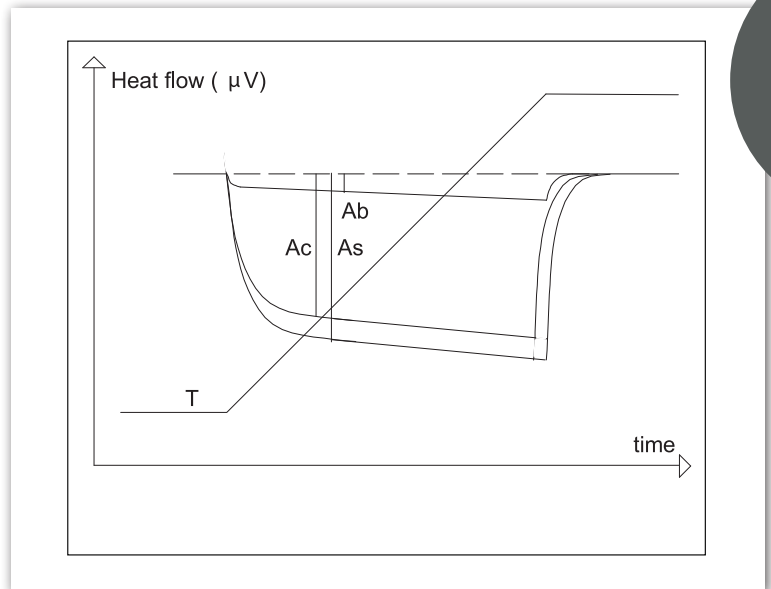


Fig. 2 : continuous method with a standard

The first run is done with the two empty crucibles (blank test), the second run with a mass m_s of sample in the measuring crucibles and the third run with a mass m_c of calibrant with a known heat capacity : C_{pc} .

Each run consists in a isotherm at a temperature T_i , a heating between the initial temperature T_i and a final temperature T_f at constant heating rate β and a isotherm at the final temperature T_f (Figure 3).

If A_b , A_s and A_c are the of the Heatflow signal measured with the blank, the sample and the calibrant respectively, the value of specific heat capacity C_p is :

$$C_p = C_{pc} \times \frac{m_c \times (A_s - A_b)}{m_s \times (A_c - A_b)} \quad (2)$$

with C_p and C_{pc} in $J.g^{-1}.K^{-1}$ A_b , A_s and A_c in μV m_s and m_c in g

Notices :

- The amplitudes may be expressed in an arbitrary unit.
- The isothermal sections of the curves must be long enough in order to obtain a stable signal before and after each ramp.

Correction of curves :

Experimentally, the isothermal sections of the curves are not adjusted to on the heatflow signal at T_i and T_f as it is presented on Figure 1 or Figure 2. For this reason, the Calisto software package for C_p determination will first correct each experimental curve (sample, blank and standard material) by replacing the original amplitude A by the corresponding difference $A-A'$ (Figure 3) before applying formula (1) or formula (2). This correction from the dotted line is performed for the two isothermal sections and the ramp.

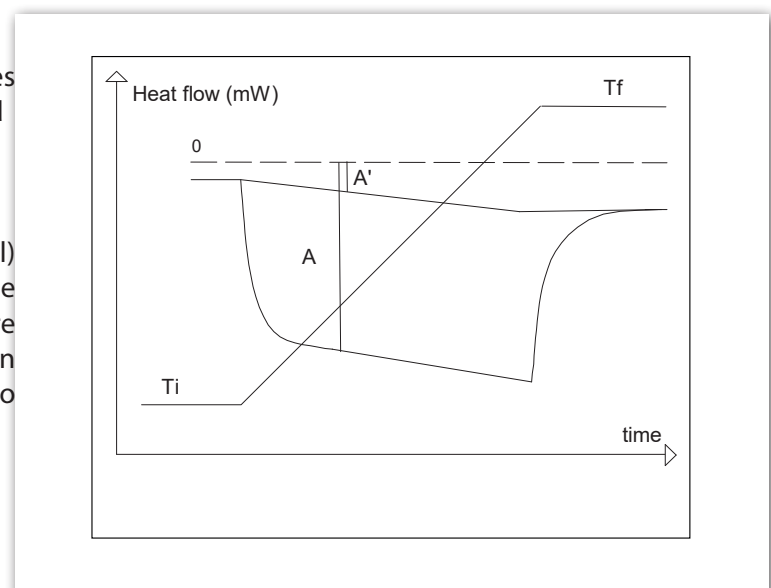


Fig. 3 : correction of curves

2. Stepwise method

This method allows for more accurate Cp measurements but leads to longer experiments.

Instruments calibrated by Joule effect effect (3D CALVET type sensor) :

It applies only to instruments calibrated by Joule effect such as CALVET, CALVET PRO, CALVET CRYO, MICROCALVET, MICROCALVET ULTRA.

The method consists in performing two runs with two vessels : one vessel in measuring side, one vessel in reference side. The first run is performed with the two empty vessels (blank test), the second run with a mass m_s of sample in the measuring vessel.

Each run consists in successive temperature increments (ΔT) performed at a given heating rate β . After each increment a waiting period is programed in order to obtain a stable signal (Figure 4). Each curve presents the shape of a succession of crenels which are automatically integrated (see Integration of crenels).

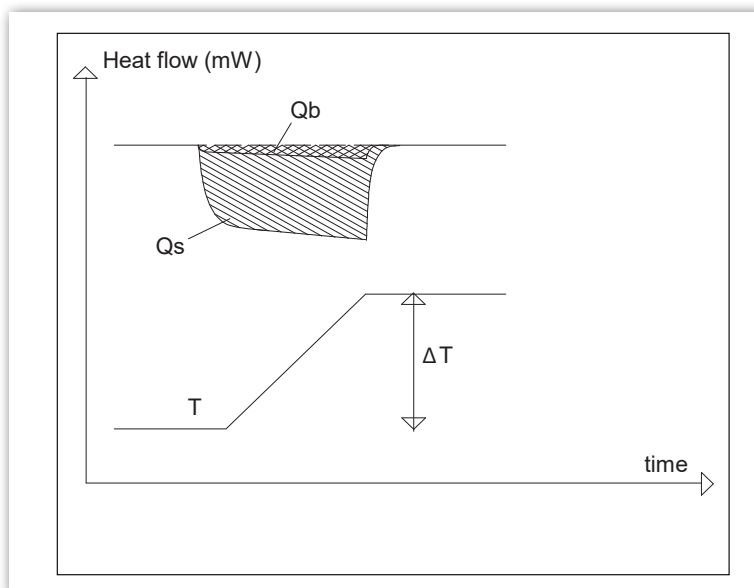


Fig. 4 : step method

If Q_b and Q_s are the measured heats (mJ) for the blank and sample respectively, the value of average specific heat capacity on the temperature increment at the average temperature is :

$$\overline{C_p} = \frac{Q_s - Q_b}{m_s \times \Delta T} \quad (3)$$

with C_p in $J g^{-1} K^{-1}$ Q_s and Q_b in J m_s in g ΔT in K

Instruments calibrated by a standard material :

Other types of instruments such as SETLINE DSC, THEMYS ONE, THEMYS and other analyzers based on plate DSC are usually calibrated by the melting of standards. This method of calibration is suitable for thermal events such as melting or phase transition but is generally not accurate enough for C_p evaluation.

In the case of C_p determination, the calibration must be done by using a standard material with a known heat capacity.

In such a case, the method consists in performing three runs with two crucibles : one measuring crucible, one reference crucible. The first run is performed with the two empty crucibles (blank test), the second run with a mass m_s of sample in the measure crucible and the third run with a mass m_c of standard material with a known heat capacity : C_{pc} .

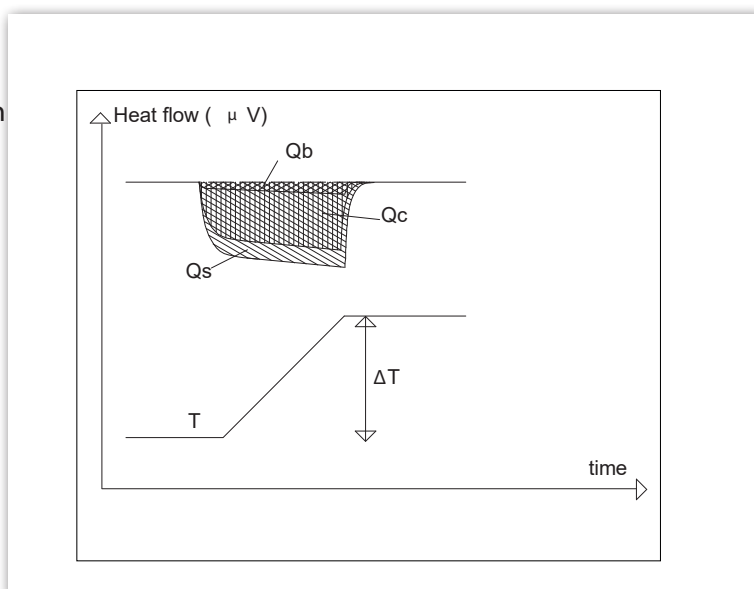


Fig. 5 : step method with a standard

Each run consists in successive temperature increments (ΔT) performed at a given heating rate β . After each increment, a waiting period is programed in order to obtain a stable signal (Figure 5). Each curve presents the shape of a succession of crenels which are automatically integrated.

If Q_b , Q_s and Q_c are the measured heats ($\mu V \cdot s$) of blank, sample and standard materials respectively, the value of average specific heat capacity $\overline{C_p}$ on the temperature increment at the average temperature is :

$$\overline{C_p} = C_{pc} \times \frac{m_c \times (Q_s - Q_b)}{m_s \times (Q_c - Q_b)} \quad (4)$$

with C_p in $J \cdot g^{-1} \cdot K^{-1}$ Q_b , Q_s and Q_c in $\mu V \cdot s$ m_s and m_c in g

Notice :

- The heats Q may be expressed in an arbitrary unit.
- The values of temperature increments have no effect on the result, provided that the same values are used for the three experiments.

Integration of crenels :

The determination of C_p by the step method implies the integration of crenel-shaped heat flow curves.

For all temperatures increments, value of temperatures T_i and T_f , the heat flow signal will be stabilized at different values. To take into account these differences, the straight line between the two successive isotherms is chosen as the baseline for each crenel integration (Figure 6).

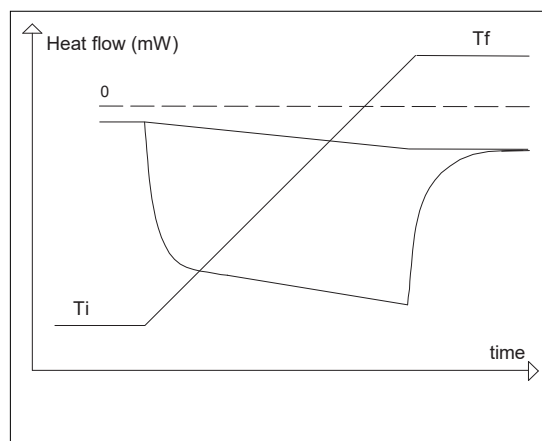


Figure 6 : integration of crenels

3. Heat capacity of liquids

Specific heat capacity of liquids :

The specific heat capacity of liquids can be determined with all the methods previously described. The experiments must be performed in batch vessels which are perfectly tight.

The analysis must be carried out with the smallest dead volume in order to reduce the evaporation of liquid. With such precautions, the incidence of the evaporation can generally be considered as negligible. It is also possible to correct the evaporation factor if both the heat of evaporation and the vapour pressure are known.

Volumic heat capacity of liquids :

To avoid the presence of vapour inside the vessel, a " liquid heat capacity vessel " has been designed for the CALVET and the CALVET CRYO. The vessel may be totally filled with liquid through a pipe. The volumic heat capacity is therefore determined. For better accuracy, the step method is recommended, and as the volume of the vessel is not known accurately, a standard material is used.

The method consists in performing three runs with two vessels : one measuring vessel, one reference vessel. The first run is carried out with the two empty vessels (blank test), the second run with the measuring vessel filled with the sample liquid and the third run with the measuring vessel filled with calibrant (or reference) liquid with a known volumic heat capacity C_{pvc} .

Each run consists in successive temperature increments (ΔT) performed at a given heating rate β . After each increment, a waiting period is observed in order to obtain a stable signal (Figure 5). Each curve presents the shape of a succession of crenels which are automatically integrated (see § 2).

If Q_b , Q_s and Q_c are the measured heats (J) of blank, sample and calibrant respectively, the value of average volumic heat capacity $\overline{C_{pv}}$ on the temperature increment at the average temperature is :

$$\overline{C_{pv}} = C_{pv_c} \times \frac{Q_s - Q_b}{Q_c - Q_b} \quad (5)$$

with C_{pv} in $J.mL^{-1}.K^{-1}$ Q_b , Q_s and Q_c in J

Notices :

- The heats Q can be expressed in an arbitrary unit.
- The values of temperature increments have no effect on the results, provided that the same values are used for the three experiments.
- The volumic heat capacity of a liquid must be divided by its density in order to obtain the corresponding specific heat capacity.

4. Drop method

This method can be used with CALVET DC and CALVET DC ALEXSYS, when specifically equipped with a sample introducer.

If a sample with a mass m_1 is dropped from a sample introducer where the temperature is T_0 to the heart of the calorimeter where the temperature is T_1 , the calorimeter will record a peak with an integral value corresponding to :

$$H_1 = \int_{T_0}^{T_1} m_1 C_p dT = m_1 \int_{T_0}^{T_1} C_p dT$$

If the same sample with a mass m_2 is dropped from a sample introducer where the temperature is T_0 to the heart of the calorimeter where the temperature is T_2 , the calorimeter will record a peak with an integral value corresponding to :

$$H_2 = \int_{T_0}^{T_2} m_2 C_p dT = m_2 \int_{T_0}^{T_2} C_p dT$$

By difference it is possible to access to the average specific heat capacity $\overline{C_p}$ within the temperature interval $[T_1, T_2]$:

$$\overline{C_p} = \left(\frac{H_2}{m_2} - \frac{H_1}{m_1} \right) \times \frac{1}{T_2 - T_1} \quad (6)$$

with C_p in $J.g^{-1}.K^{-1}$ H_1 and H_2 in J m_1 and m_2 in g T_1 and T_2 in K

For this method, the calorimeters are generally calibrated by the drop of a standard material with a known heat capacity.